

AD-A092 997

PENNSYLVANIA STATE UNIV UNIVERSITY PARK  
ENHANCED HIGH TEMPERATURE ADSORPTION IN TERNARY SYSTEMS.(U)  
NOV 80 6 SIMKOVICH

F/6 7/2

DAAG29-77-6-0115

UNCLASSIFIED

ARO-14510.2-MS

NL

1 of 1  
AD-A092 997

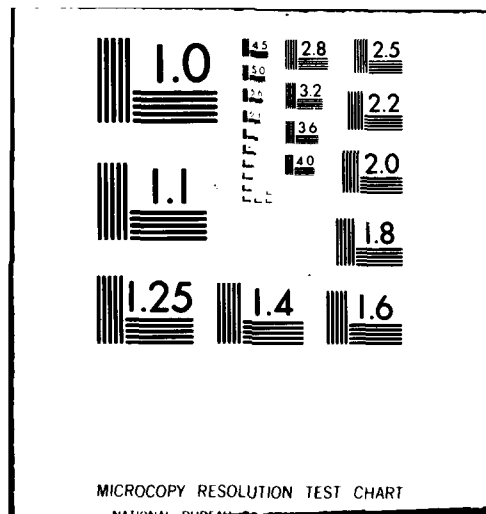
END

DATE

FILED

1-81

DTIC



AD A 092997

DDC FILE COPY

UNCLASSIFIED  
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 14510.2-MS	2. GOVT ACCESSION NO. AD-A092997	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Enhanced High Temperature Adsorption in Ternary Systems		5. TYPE OF REPORT & PERIOD COVERED Final Report 21 Mar 77 - 20 Sep 80
6. AUTHOR(s) G. Simkovich		7. CONTRACT OR GRANT NUMBER(s) DAAG29-77-G-0115
8. PERFORMING ORGANIZATION NAME AND ADDRESS Pennsylvania State University University Park, PA 16802		9. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
10. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709		11. REPORT DATE 25 Nov 80
12. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES 15
LEVEL		14. SECURITY CLASS. (of this report) Unclassified
15. DECLASSIFICATION/DOWNGRADING SCHEDULE		
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) NA		
18. SUPPLEMENTARY NOTES The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) adsorption                      chromium alloys ternary systems              oxides iron                              oxygen iron alloys		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Adsorption was studied in the Fe-Cr-O system at 1313K. H <sub>2</sub> /H <sub>2</sub> O atmospheres were utilized to control the oxygen pressures. Alloy compositions ranged from pure iron to chromium concentrations of 2 w/o.		

80 1212 126

Final Report

by

"Enhanced High Temperature Adsorption in Ternary Systems"

ARO Proposal Number DRXRO-PR P-14510-MS  
Contract or Grant Number DAAG29-77-G-0115  
Name of Institution The Pennsylvania State University

Author of Report

G. Simkovich  
G. Simkovich, Professor of Metallurgy

Date of Report

25 November 1980

Accession For	
NTIS GRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A	

### Statement of the Problem

The basic experimental approach to the research undertaken was to determine adsorption in a ternary system which would permit evaluation of the thermodynamic relation

$$\Gamma_3 \approx \left[ \frac{\left( \frac{\partial \sigma}{\partial \ln y_3} \right)}{RT(1 + \epsilon_3 y_3)} - \frac{\Gamma_3 \epsilon_{23} \Gamma_2}{(1 + \epsilon_3 y_3)} \right] y_2 \rightarrow 0 \quad (1a)$$

and

$$\Gamma_2 \approx \left[ \frac{\left( \frac{\partial \sigma}{\partial \ln y_2} \right)}{RT(1 + \epsilon_2 y_2)} - \frac{y_2 \epsilon_{23} \Gamma_3}{(1 + \epsilon_2 y_2)} \right] y_3 \rightarrow 0 \quad (1b)$$

derived by Darken and Simkovich (attached paper defines the symbols). The system Fe-Cr-O at 1313K (1040°C) was chosen and H<sub>2</sub>/H<sub>2</sub>O atmospheres were utilized to control the oxygen pressures. Alloy compositions ranged from pure iron to chromium concentrations of two wt %.

### Results

Utilizing a thermostated automatic recording microbalance the adsorption of oxygen on the pure iron and the iron-chromium alloys was measured. These tests are still in progress; however, typical results are depicted in Fig. 1. It may be noted that in accord with  $\epsilon_{Cr-O}$  as a negative interaction coefficient the adsorption of oxygen on iron-chromium alloys is anticipated to be greater than the adsorption of oxygen on pure iron. Such is revealed in Fig. 1.

The adsorption curves shown in Fig. 1 are based on the premise that little oxygen dissolves in the iron or iron based alloy. This is not true and

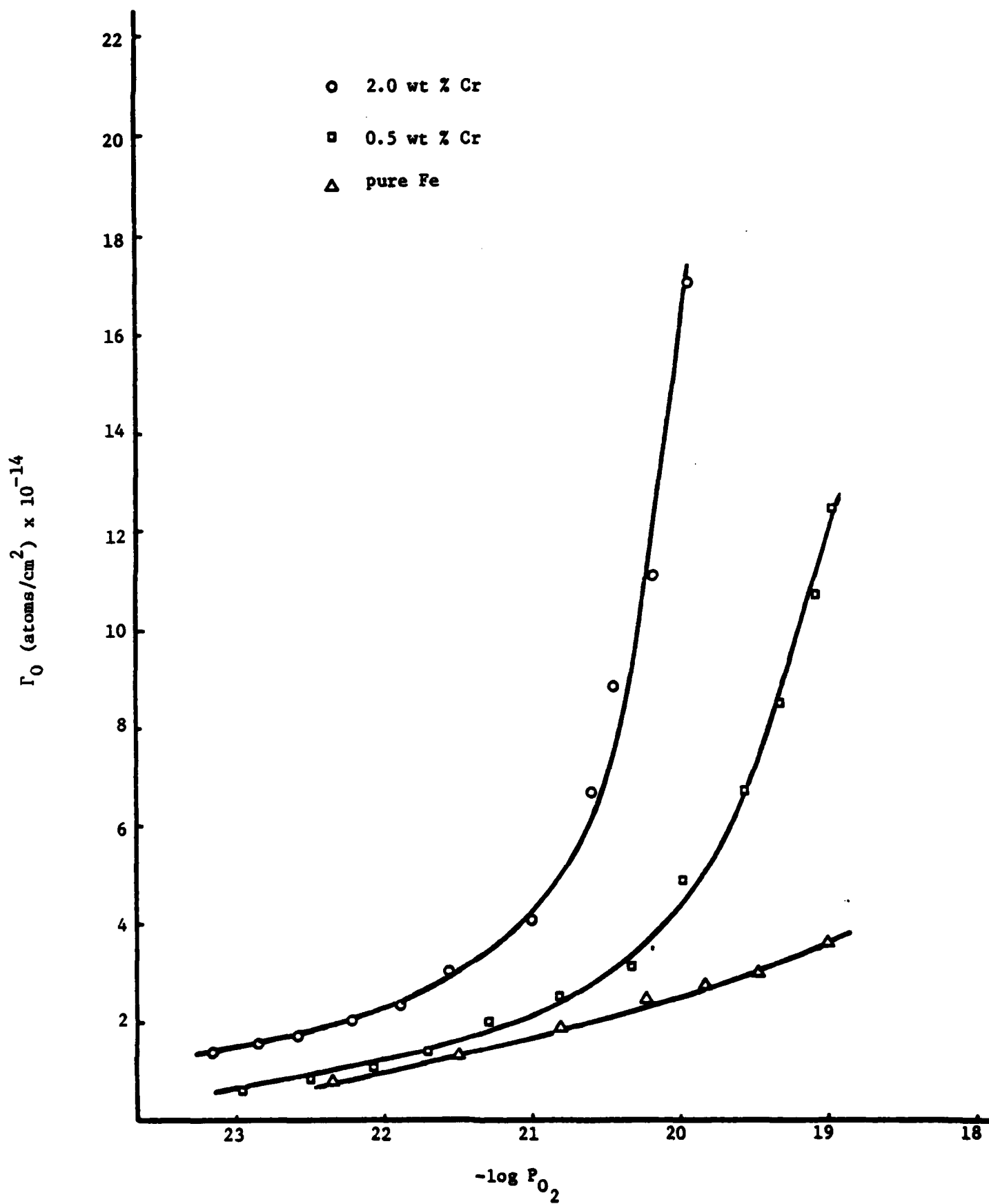


Figure 1. Adsorption of Oxygen on Pure Iron and Iron-Chromium Alloys at 1313K.

therefore the solubility of oxygen in pure iron and iron-chromium alloys is being measured on small surface area samples. Typical values obtained on a 1 wt. % Cr alloy are given in Table I. These measurements are also being continued and in addition to providing solubility data such measurements also permit the evaluation of the interaction coefficient  $\epsilon_{23}$ , or  $\epsilon_{\text{Cr-O}}$  in this case.

Table I. Solubility of Oxygen in Fe-1 wt % Cr Alloy at 1313K (1040°C)

$P_{\text{O}_2}$ (atm)	$-\log P_{\text{O}_2}$	$P_{\text{O}_2}^{1/2}$ (atm) <sup>1/2</sup>	$\frac{\text{gm of oxygen}}{\Sigma \text{ wt of Fe, Cr and O, gms}}$
$9.23 \times 10^{-22}$	21.03	$3.04 \times 10^{-11}$	$3.50 \times 10^{-7}$
$1.78 \times 10^{-21}$	20.75	$4.22 \times 10^{-11}$	$5.83 \times 10^{-7}$
$4.87 \times 10^{-21}$	20.31	$6.98 \times 10^{-11}$	$9.33 \times 10^{-7}$
$8.46 \times 10^{-21}$	20.01	$9.20 \times 10^{-11}$	$1.40 \times 10^{-6}$
$1.33 \times 10^{-20}$	19.88	$1.15 \times 10^{-10}$	$1.63 \times 10^{-6}$
$3.83 \times 10^{-20}$	19.47	$1.96 \times 10^{-10}$	$2.80 \times 10^{-6}$

The results listed in Table I fit, reasonably well, a Siverts' type plot.

In addition to the solubility and adsorption measurements discussed above Auger spectroscopic determinations have been made on a number of samples. Some of these results were given in the report for the time period 1 January 1980-30 June 1980. Further studies have been made so that we shall have Auger results on 0.25, 0.50, 1.00, 1.50 and 2.00 wt % Cr alloys, before and after chemisorption of oxygen.

The initial Auger results are in accord with the derived theory for adsorption in multicomponent systems. They also indicate that adsorption in the Fe-Cr-O system is not confined to a few atomic layers at the alloy-gas interface but occurs to a depth of at least 40 Angstroms.

It is perhaps appropriate to remark that, following some initial experimental problems, the project has consistently provided new and interesting data which, it is anticipated, will be utilized, along with the theories developed, as a basis to predict adsorption phenomena in multicomponent systems.

#### Publications

Two papers have been published - "High Temperature Adsorption in Ternary Systems" by L. S. Darken and G. Simkovich in Scripta Met., 13, 431 (1979) and "An Analysis of Chemisorption in Multicomponent Systems" by B. Ozturk and G. Simkovich to be published in Met. Trans. A., Dec. (1980). These are attached.

Another paper, "Adsorption in Multicomponent Systems" is to be presented at the Carl Wagner Commemorative Symposium at the AIME Meeting in Feb., 1981 in Chicago, Ill. The AIME will published these symposium papers in a Special Symposium Volume. This paper is authored by B. Ozturk and G. Simkovich.

At least two additional papers by B. Ozturk and G. Simkovich will be prepared. These are tentatively titled "Chemisorption of Oxygen on Fe-Cr Alloys at 1313K" and "The Solubility of Oxygen in Fe-Cr Alloys and the Interaction Coefficient,  $\epsilon_{Cr-O}$ , at 1313K."

#### Scientific Personnel

##### Principal Investigators

Prof. L. S. Darken (deceased, 7 June 1978).  
Prof. G. Simkovich

##### Graduate Students

H. S. Hsu - M.S. Degree, 1979  
B. Ozturk - pH.D. Degree in 1981  
M. H. Lee - Ph.D. Degree in 1981-82



## HIGH TEMPERATURE ADSORPTION IN TERNARY SYSTEMS

L. S. Darken\* and G. Sinkovich\*\*

\*Deceased-At the time of his death Dr. Darken was with the Department of Geosciences, The Pennsylvania State University, University Park, PA 16802.

\*\*206-B Steidle Building, Metallurgy Section, Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802.

(Received December 11, 1978)  
(Revised April 5, 1979)

Adsorption at interfaces, significant in many systems, has been studied primarily in binary systems, even though real systems are primarily multicomponent systems. In binary systems, adsorption, especially at high temperatures, is of the order of a monolayer or less. In multicomponent systems, however, surface adsorption, under certain conditions of composition and temperature, may reasonably be expected to be much more extensive than in binary systems containing the same major component as is shown in the following section.

As an example, one might consider the adsorption of oxygen on pure silver, in one case, and on silver alloyed with small amounts of an alloying element which has a higher affinity for oxygen than does silver, say copper, in the second case. For the case of oxygen on pure silver (1), it is relatively well established that a monolayer of oxygen is adsorbed at 932°C and oxygen pressures between 10.1 and 10,100 Pa. In the case Ag-Cu alloys one may anticipate that copper from the alloy is adsorbed at the surface at a lower  $P_{O_2}$  than that for formation of an oxide phase and induces further adsorption of oxygen; these processes may reasonably be expected to repeat, giving rise to multilayer adsorption of both oxygen and copper. It is noted that this enhancement of oxygen and copper adsorption is quite different from the BET type (2).

We develop, in the following section, the relations which indicate that multilayer adsorption is also to be anticipated from a quantitative point of view, as well as the qualitative concept presented in the above introduction.

## Theoretical

We first consider a binary system, say "pure" metal (component 1, solid adsorbent) and "pure" gas (component 2, adsorbate). A "clean" specimen of the metal phase exposed to the gas phase at a chemical potential less than that necessary to form an intermediate phase will dissolve an equilibrium amount of the gaseous component in solid solution and will adsorb on its surface an amount of gas [generally, less than a monolayer (1,3-6), but not necessarily less than a monolayer (7)] in accord with the Gibbs adsorption equation (7) for a binary system

$$\Gamma_2 = - \left( \frac{\partial \sigma}{\partial \mu_2} \right)_T = - \frac{1}{RT} \left( \frac{\partial \sigma}{\partial \ln a_2} \right)_T \quad (1)$$

where  $\sigma$  is the surface free energy of the system,  $\mu_2$  is the chemical potential of the gaseous component,  $a_2$  is the thermodynamic activity of this component,  $R$  and  $T$  carry their normal connotation and  $\Gamma_2$  is the excess concentration of component 2, in respect to component 1, adsorbed at the interface. In the Gibbs adsorption relation, eq. 1, no assumption is involved concerning the amount of adsorbate (7), thus although experiments which were performed with care normally find an excess concentration,  $\Gamma_2$  in binary systems of the order corresponding to a monolayer or less of component 2, it is entirely feasible that multilayers may be formed.

We now consider the addition of a third component to the metal phase. Further, we take this third component to have a high "affinity" for the gaseous phase and we consider adsorption only at the gas-solid interface at this time although adsorption at other interfaces,

e.g. grain boundaries, could well be included in the analysis. For this case, exposure of the metal phase to the gaseous phase results in (i) dissolution of the gas in the metal phase; (ii) adsorption of component 3, probably in multilayers at the metal phase-gas interface; and (iii) adsorption of the gas, component 2, probably in multilayers, also at the metal-gas interface. The multilayer adsorption occurs primarily because of the "affinity" which components 2 and 3 have for each other. Again, of course, the activities of the components are maintained, such that no new condensed phase is formed.

Following C. Wagner's (8) recent thermodynamic analysis of adsorption we use, as independent variable, bulk composition terms  $y_i$ , defined as

$$y_i = n_i/n_1 \quad (2)$$

where compositions, therefore, are expressed relative to component 1 and  $n_i$  are moles of component  $i$  in the bulk alloy. We restrict the analysis to the single, planar solid phase present and we consider  $A$ ,  $T$ ,  $P$  (or  $V$ ) and  $n_1$  to be constant. Under these conditions for a ternary system, the Gibbs adsorption equation becomes

$$d\sigma = -\Gamma_2 du_2 - \Gamma_3 du_3 \quad (3)$$

We now introduce the derivatives of the chemical potentials with respect to  $y_i$  [at constant  $A$ ,  $T$ ,  $P$  (or  $V$ ), and  $y$ 's  $\neq y_i$ ]

$$-\frac{\partial \sigma}{\partial y_2} = \Gamma_2 \left( \frac{\partial u_2}{\partial y_2} \right) + \Gamma_3 \left( \frac{\partial u_3}{\partial y_2} \right) \quad (4a)$$

$$-\frac{\partial \sigma}{\partial y_3} = \Gamma_2 \left( \frac{\partial u_2}{\partial y_3} \right) + \Gamma_3 \left( \frac{\partial u_3}{\partial y_3} \right) \quad (4b)$$

Utilizing the relation

$$\frac{\partial u_i}{\partial y_j} = RT \left( \frac{\partial \ln a_i}{\partial y_j} \right) \quad (5)$$

in order to express (4) in terms of activities one obtains, upon solving for  $\Gamma_2$  and  $\Gamma_3$ , the relations,

$$\Gamma_2 = -\frac{1}{RT} \frac{\left( \frac{\partial \sigma}{\partial y_3} \right) \left( \frac{\partial \ln a_3}{\partial y_2} \right) - \left( \frac{\partial \sigma}{\partial y_2} \right) \left( \frac{\partial \ln a_3}{\partial y_3} \right)}{\left( \frac{\partial \ln a_2}{\partial y_2} \right) \left( \frac{\partial \ln a_3}{\partial y_3} \right) - \left( \frac{\partial \ln a_3}{\partial y_2} \right) \left( \frac{\partial \ln a_2}{\partial y_3} \right)} \quad (6a)$$

$$\Gamma_3 = -\frac{1}{RT} \frac{\left( \frac{\partial \sigma}{\partial y_2} \right) \left( \frac{\partial \ln a_2}{\partial y_3} \right) - \left( \frac{\partial \sigma}{\partial y_3} \right) \left( \frac{\partial \ln a_2}{\partial y_2} \right)}{\left( \frac{\partial \ln a_2}{\partial y_2} \right) \left( \frac{\partial \ln a_3}{\partial y_3} \right) - \left( \frac{\partial \ln a_3}{\partial y_2} \right) \left( \frac{\partial \ln a_2}{\partial y_3} \right)} \quad (6b)$$

We define, for the bulk alloy, the "activity coefficients" as

$$\gamma_i = \frac{a_i}{y_i} \quad (7)$$

and

$$\epsilon_i = \frac{\partial \ln \gamma_i}{\partial y_i} \quad (8)$$

and

$$\epsilon_{ij} = \frac{\partial \ln \gamma_i}{\partial y_j} = \frac{\partial \ln \gamma_j}{\partial y_i} \quad (9)$$

where  $\epsilon_1$  and  $\epsilon_{1j}$  are comparable to the self-interaction and interaction coefficients presently found in the metallurgical literature (9). Utilizing eqs. (7), (8) and (8), eqs. (6) become

$$\Gamma_2 = -\frac{1}{RT} \frac{\left[ \frac{\partial \sigma}{\partial \ln y_2} (1 + \epsilon_3 y_3) - \frac{\partial \sigma}{\partial \ln y_3} (y_2 \epsilon_{23}) \right]}{(1 + \epsilon_2 y_2) (1 + \epsilon_3 y_3) - (\epsilon_{23}^2 y_2 y_3)} \quad (10a)$$

$$\Gamma_3 = -\frac{1}{RT} \frac{\left[ \frac{\partial \sigma}{\partial \ln y_3} (1 + \epsilon_2 y_2) - \frac{\partial \sigma}{\partial \ln y_2} (y_3 \epsilon_{23}) \right]}{(1 + \epsilon_2 y_2) (1 + \epsilon_3 y_3) - (\epsilon_{23}^2 y_2 y_3)} \quad (10b)$$

Eqs. (10) are general, at the stated conditions, as no approximations have been made in arriving at the expressed relations. In particular, no approximations as to the type of solution, i.e. ideal or regular have been made and, therefore, the derived relations may be considered for many ternary systems.

We now consider the special case of low solubility of component 2, e.g., oxygen or sulfur, in the alloy phase. We, therefore, consider  $y_2$  to be so small that all terms containing  $y_2$  may be set equal to zero. Eqs. (10) then become

$$\Gamma_2 = -\frac{1}{RT} \left( \frac{\partial \sigma}{\partial \ln y_2} \right) \quad (11a)$$

$$\Gamma_3 = -\frac{1}{RT} \frac{\left[ \frac{\partial \sigma}{\partial \ln y_3} - y_3 \epsilon_{23} \left( \frac{\partial \sigma}{\partial \ln y_2} \right) \right]}{1 + \epsilon_3 y_3} \quad (11b)$$

Substituting eq. (11a) into (11b) and rearranging one obtains

$$\Gamma_3 = -\frac{1}{RT} \frac{\frac{\partial \sigma}{\partial \ln y_3}}{(1 + \epsilon_3 y_3)} - \frac{y_3 \epsilon_{23} \Gamma_2}{(1 + \epsilon_3 y_3)} \quad (12a)$$

Eq. (12) indicates quite strongly that the presence of component 2 may enhance to a great extent the adsorption of component 3 at the solid alloy-gas interface if  $\epsilon_{23}$  has a large negative value, as is the normal case for an element which has a high "affinity" for another element; in this case and if  $\Gamma_2$  is sufficiently large, the second term on the right of eq. (12) becomes a large positive term that may reasonably be expected to contribute significantly to  $\Gamma_3$ . Conversely, if  $\epsilon_{23}$  is a large positive number then desorption will occur in the ternary system.

Since eqs. (10) are symmetrical with respect to  $\Gamma_2$  and  $\Gamma_3$  one may obtain an equation similar to eq. (12a) for  $\Gamma_2$  whenever the solubility of component 3 is allowed to go to zero. In this case one obtains, as an analogue to eq. (12a), the relation

$$\Gamma_2 = -\frac{1}{RT} \frac{\frac{\partial \sigma}{\partial \ln y_2}}{(1 + \epsilon_2 y_2)} - \frac{y_2 \epsilon_{23} \Gamma_3}{(1 + \epsilon_2 y_2)} \quad (12b)$$

Again, the adsorption of a component, 2, is shown to be enhanced by the presence of another component, 3, which has a special attraction for the component as would be exhibited by a large negative value of  $\epsilon_{23}$ .

In catalytic investigations (10-13) it is relatively well accepted that the composition of a binary alloy is surface enriched in one of the binary alloy components when the alloy is exposed to a gaseous atmosphere which has a particularly high affinity for this component. These results are completely in accord with our theoretical expressions.

A few systems that have shown such behaviour are Ni-Au (12) and Au-Pt (10) alloys. When Ni-Au alloys are exposed to oxygen pressures of the order of  $10^{-3}$  to  $10^{-5}$  Pa for short periods

THIS PAGE IS BEST QUALITY PRACTICALLY  
FROM CONFIDENTIAL AND TO BDC

of time, of the order of several hundred seconds, over a range of temperatures from room temperature, for most of the reported experiments, to 1300 K, for some experiments, it was found that the alloys which were initially gold enriched in inert atmospheres or hydrogen, in accord with Gibbs' equation for the adsorption of a lower surface energy element ( $\sigma_{Au} = 1.40 \text{ J/m}^2$  <  $\sigma_{Ni} = 1.85 \text{ J/m}^2$ ) became nickel enriched in accord with the derived relations. Furthermore, Au-Pt alloys which are gold enriched under ultrahigh vacuum conditions, again in accord with Gibbs' equation for binary systems ( $\sigma_{Au} = 1.40 \text{ J/m}^2$  <  $\sigma_{Pt} = 2.35 \text{ J/m}^2$ ), become surface enriched in platinum upon exposure to CO of about  $10^{-3}$  to  $10^{-2}$  Pa for relatively long periods of time (a few hours to three plus days) from room temperature to 373 K.

In the case of the Ni-Au alloys one, of course, has the possibility of actually oxidizing the nickel from the alloy even at the low oxygen pressures utilized but the Au-Pt alloys should not exhibit any such behavior. Thus, it is apparent that the results obtained are in general agreement with the above derived relations, in particular eqs. (12a) and (12b).

It is important to realize the  $c_{23}$  need not always carry a negative sign and thus enhance adsorption but may also carry a positive sign and, hence, reduce adsorption. In particular it is known that  $c_{23}$  carries a positive sign for sulfur and nitrogen and for sulfur and carbon dissolved in liquid iron. On this basis one would anticipate that the presence of nitrogen or carbon in liquid iron and, assuming that the sign of  $c_{23}$  does not change with a decrease in temperature, also in solid iron would decrease the adsorption of sulfur, a highly "surface active" agent in iron, at interfaces. Some recent studies (14) by Tauber and Grabke of surface concentrations of fracture surfaces of Fe-S-N and of Fe-S-C alloys show that both nitrogen and carbon displace sulfur at interfaces when they are present in sufficiently high concentrations at 600°C.

Hence, both enhancement and reduction of adsorption is attainable which is completely in accord with the derived relations.

In addition, recent experiments at Penn State (15) have shown that the presence of small amounts of Cr in Fe enhances considerably the adsorption of oxygen upon these alloys in comparison to adsorption upon "pure iron".

Support by the U.S. Army Research Office is gratefully acknowledged.

#### References

1. F. R. Buttner, H. Udin and J. Wulff, *J. Phys. Chem.* **56**, 557 (1952).
2. W. W. Adamson, "Physical Chemistry of Surfaces", Interscience Publ., Inc., N.Y., pp. 475 ff. (1960).
3. P. Kozakevitch and G. Urbain, *Mem. Sci. Rev. Met.*, **58**, 932 (1961).
4. E. D. Hondros, *Proc. Roy. Soc. A* **286**, 297 (1965).
5. D. R. Stickley, J. P. Hirth, G. Mayrick and R. Speiser, *Trans. AIME*, **7A**, 71 (1976).
6. C. E. Bauer, R. Speiser and J. P. Hirth, *Trans. AIME* **7A**, 75 (1976).
7. J. W. Gibbs, *Collected Works*, Vol. I, pp. 219 ff., Yale University Press, New Haven, CT (1948).
8. C. Wagner, *Nachrichten der Akademie der Wissenschaften in Göttingen*, II. Math.-Physik. Klasse, Nr. 3, 37 (1973).
9. J. F. Elliott, M. Gleiser, and V. Ramakrishna, "Thermochemistry for Steelmaking", Vol. II, Addison-Wesley Publ. Co., Inc., pp. 565 ff. (1963).
10. R. Bouvman and W. M. H. Sachtler, *J. Catal.* **19**, 127 (1970).
11. R. Bouvman, G. J. Lippits and W. M. H. Sachtler, *J. Catal.* **25**, 350 (1972).
12. F. L. Williams and M. Boudart, *J. Catal.* **30**, 438 (1973).
13. W. M. H. Sachtler and R. A. Van Santen, in "Advances in Catal.", (ed. by D. D. Cley, H. Pines and F. B. Weiss) Academic Press, N.Y., **26**, 69 (1977).
14. G. Tauber and H. J. Grabke, *Ber. Bunsenges Phys. Chem.* **82**, 298 (1978).
15. H. S. Hsu and G. Simkovich, research in progress, The Pennsylvania State University, University Park, PA 16802.

Accepted for Publication in Met. Trans. A, Dec. (1980).

## "An Analysis of Chemisorption in Multicomponent Systems"

B. Ozturk and G. Simkovich

### Introduction

The mechanical and corrosive properties of many polycrystalline materials frequently are influenced substantially by adsorption of minor solute components at grain boundaries and other interfaces. Unfortunately, because theoretical analyses have primarily been restricted to binary systems, most experimental efforts have necessarily interpreted results under restrictive theoretical foundations.

Recently, Darken and Simkovich<sup>1</sup>, following Wagner<sup>2</sup>, obtained theoretical relations for adsorption in ternary systems which may be utilized to predict either enhanced or reduced adsorption in such systems. This note is concerned with the extension of Darken and Simkovich's analysis of ternaries to multicomponent systems and indicates how the derived relations may be employed to indicate the course of adsorption as solutes are added or extracted from a solvent phase.

### Theoretical

For a binary system at equilibrium at constant temperature and pressure and where no strain energy is involved, e.g., at free interfaces or incoherent grain boundaries, the Gibbs adsorption equation is,

$$\Gamma_2 = - \left( \frac{\partial \sigma}{\partial \mu_2} \right) = - \frac{1}{RT} \left( \frac{\partial \sigma}{\partial \ln a_2} \right)_T \quad (1)$$

---

B. Ozturk and G. Simkovich are Graduate Student and Professor of Metallurgy, respectively, in the Metallurgy Section, Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802

where  $\sigma$  is the surface free energy of the system,  $\mu_2$  is the chemical potential of component 2 (the solvent is taken as component 1),  $a_2$  is the thermodynamic activity of component 2,  $R$  and  $T$  carry their normal connotation and  $\Gamma_2$  is the excess concentration of component 2, with respect to component 1, adsorbed at the interface. Following Wagner<sup>2</sup>,  $\Gamma_2$  is defined explicitly as the difference between the concentration of component 2 in the surface region and the concentration of component 2 in the bulk phase where the concentrations are related only to the main component 1 (see eq. 3). It should be noted that the Gibbs adsorption relation is not restrictive in terms of the amount of material adsorbed nor the spatial extent of adsorption<sup>3</sup>.

Utilizing, for a ternary system, the relation

$$d\sigma = -\Gamma_1 d\mu_2 - \Gamma_3 d\mu_3 \quad (2)$$

and the definitions

$$y_i = n_i/n_1 \quad \text{bulk composition} \quad (3)$$

$$\gamma_i = a_i/y_i \quad \text{"activity coefficient"} \quad (4)$$

$$\epsilon_i = \frac{\partial \ln \gamma_i}{\partial y_i} \quad \text{self-interaction coefficient} \quad (5)$$

$$\epsilon_{ij} = \frac{\partial \ln \gamma_i}{\partial y_j} = \frac{\partial \ln \gamma_j}{\partial y_i} \quad \text{interaction coefficient} \quad (6)$$

Darken and Simkovich obtained the relations

$$\Gamma_3 = - \left[ \frac{\left( \frac{\partial \sigma}{\partial \ln y_3} \right)}{RT(1 + \epsilon_3 y_3)} - \frac{y_3 \epsilon_{23} \Gamma_2}{(1 + \epsilon_3 y_3)} \right] \quad y_2 \rightarrow 0 \quad (7a)$$

and

$$\Gamma_2 = - \left[ \frac{\left( \frac{\partial \sigma}{\partial \ln y_2} \right)}{RT(1 + \epsilon_2 y_2)} - \frac{y_2 \epsilon_{23} \Gamma_3}{(1 + \epsilon_2 y_2)} \right] \quad y_3 \rightarrow 0 \quad (7b)$$

with  $A$  (area),  $T$ ,  $P$  (or  $V$ ) and  $y$ 's  $\neq y_1$  held constant.

We consider the case of a quaternary system. For this case Eq. (2) becomes

THIS PAGE IS FROM THE ORIGINAL DOCUMENT FROM COPY 10

$$d\sigma = -\Gamma_2 du_2 - \Gamma_3 du_3 - \Gamma_4 du_4 \quad (8)$$

Introducing the derivatives of the chemical potentials with respect to  $y_1$  [at constant A, T and P (or V)] one obtains the set of equations

$$-\frac{\partial \sigma}{\partial y_1} = \Gamma_2 \frac{\partial \mu_2}{\partial y_1} + \Gamma_3 \frac{\partial \mu_3}{\partial y_1} + \Gamma_4 \frac{\partial \mu_4}{\partial y_1} \quad (9)$$

for  $y_1 = 2, 3$  or  $4$  with the other  $y$ 's held constant.

- Utilizing the relation

$$\frac{\partial \mu_1}{\partial y_j} = RT \left( \frac{\partial \ln a_1}{\partial y_j} \right) \quad (10)$$

in order to express Eq. (9) in terms of activities one obtains, upon solving for  $\Gamma_2$ , the relation

$$\Gamma_2 = -\frac{1}{RT} \left[ \frac{\left( \frac{\partial \ln a_2}{\partial y_2} \right) \left( \frac{\partial \ln a_4}{\partial y_2} \right) \left[ \left( \frac{\partial \sigma}{\partial y_3} \right) \left( \frac{\partial \ln a_3}{\partial y_4} \right) - \left( \frac{\partial \ln a_3}{\partial y_3} \right) \left( \frac{\partial \sigma}{\partial y_4} \right) \right] + \left( \frac{\partial \ln a_2}{\partial y_2} \right) \left( \frac{\partial \ln a_3}{\partial y_3} \right) - \left( \frac{\partial \ln a_3}{\partial y_2} \right) \left( \frac{\partial \ln a_2}{\partial y_3} \right)}{\left[ \left( \frac{\partial \ln a_2}{\partial y_2} \right) \left( \frac{\partial \ln a_4}{\partial y_2} \right) - \left( \frac{\partial \ln a_4}{\partial y_2} \right) \left( \frac{\partial \ln a_2}{\partial y_2} \right) \right] \left[ \left( \frac{\partial \ln a_2}{\partial y_2} \right) \left( \frac{\partial \ln a_4}{\partial y_4} \right) - \left( \frac{\partial \ln a_4}{\partial y_2} \right) \left( \frac{\partial \ln a_2}{\partial y_4} \right) \right]} + \frac{\left( \frac{\partial \ln a_2}{\partial y_2} \right) \left( \frac{\partial \ln a_4}{\partial y_3} \right) \left[ \left( \frac{\partial \sigma}{\partial y_2} \right) \left( \frac{\partial \ln a_3}{\partial y_4} \right) - \left( \frac{\partial \ln a_3}{\partial y_4} \right) \left( \frac{\partial \sigma}{\partial y_2} \right) \right] + \left( \frac{\partial \ln a_2}{\partial y_4} \right) \left( \frac{\partial \ln a_4}{\partial y_2} \right) - \left[ \left( \frac{\partial \ln a_2}{\partial y_2} \right) \left( \frac{\partial \ln a_4}{\partial y_3} \right) - \left( \frac{\partial \ln a_4}{\partial y_3} \right) \left( \frac{\partial \ln a_2}{\partial y_2} \right) \right]}{\left[ \left( \frac{\partial \ln a_2}{\partial y_2} \right) \left( \frac{\partial \ln a_4}{\partial y_2} \right) - \left( \frac{\partial \ln a_4}{\partial y_2} \right) \left( \frac{\partial \ln a_2}{\partial y_2} \right) \right] \left[ \left( \frac{\partial \ln a_2}{\partial y_2} \right) \left( \frac{\partial \ln a_4}{\partial y_4} \right) - \left( \frac{\partial \ln a_4}{\partial y_2} \right) \left( \frac{\partial \ln a_2}{\partial y_4} \right) \right]} + \frac{\left( \frac{\partial \ln a_2}{\partial y_2} \right) \left( \frac{\partial \ln a_4}{\partial y_4} \right) \left[ \left( \frac{\partial \sigma}{\partial y_3} \right) \left( \frac{\partial \ln a_3}{\partial y_2} \right) - \left( \frac{\partial \ln a_3}{\partial y_2} \right) \left( \frac{\partial \sigma}{\partial y_3} \right) \right] + \left( \frac{\partial \ln a_2}{\partial y_2} \right) \left( \frac{\partial \ln a_3}{\partial y_3} \right) - \left( \frac{\partial \ln a_3}{\partial y_2} \right) \left( \frac{\partial \ln a_2}{\partial y_3} \right)}{\left[ \left( \frac{\partial \ln a_2}{\partial y_2} \right) \left( \frac{\partial \ln a_4}{\partial y_4} \right) - \left( \frac{\partial \ln a_4}{\partial y_2} \right) \left( \frac{\partial \ln a_2}{\partial y_4} \right) \right] \left[ \left( \frac{\partial \ln a_2}{\partial y_2} \right) \left( \frac{\partial \ln a_4}{\partial y_4} \right) - \left( \frac{\partial \ln a_4}{\partial y_2} \right) \left( \frac{\partial \ln a_2}{\partial y_4} \right) \right]} \right] \quad (11)$$

Similar expressions for  $\Gamma_3$  and  $\Gamma_4$  are also obtainable.

For an  $n$  component system, Eq. (11) will be the solution of the linear system of equations with  $(n-1)$  equations and  $(n-1)$  unknowns.

We utilize Eqs. (4), (5) and (6), i.e., the activity coefficient,  $\gamma_i$ , the self-interaction coefficient,  $\epsilon_i$ , and the interaction coefficient,  $\epsilon_{ij}$ , in Eq. (11) to obtain

$$\Gamma_2 = -\frac{1}{RT} \left[ \frac{(1+y_2\epsilon_2)(y_2\epsilon_{24}) \left[ \left( \frac{\partial \sigma}{\partial \ln y_3} \right) (y_4\epsilon_{34}) - (1+y_3\epsilon_3) \left( \frac{\partial \sigma}{\partial \ln y_4} \right) \right] +}{[(1+y_2\epsilon_2)(1+y_3\epsilon_3) - (y_2\epsilon_{23})(y_3\epsilon_{23})][(1+y_2\epsilon_2)(1+y_4\epsilon_4) - (y_4\epsilon_{24})(y_2\epsilon_{24})]} \right. \\ \left. \frac{(1+y_2\epsilon_2)(y_3\epsilon_{34}) \left[ (y_2\epsilon_{23}) \left( \frac{\partial \sigma}{\partial \ln y_4} \right) - (y_4\epsilon_{34}) \left( \frac{\partial \sigma}{\partial \ln y_2} \right) \right] +}{(y_4\epsilon_{24})(y_2\epsilon_{24})} - \frac{[(1+y_2\epsilon_2)(y_3\epsilon_{34}) - (y_3\epsilon_{23})(y_2\epsilon_{24})]}{[(1+y_2\epsilon_2)(1+y_4\epsilon_4) - (y_4\epsilon_{24})(y_2\epsilon_{24})]} \right. \\ \left. \frac{(1+y_2\epsilon_2)(1+y_4\epsilon_4) \left[ (1+y_3\epsilon_3) \left( \frac{\partial \sigma}{\partial \ln y_2} \right) - (y_2\epsilon_{23}) \left( \frac{\partial \sigma}{\partial \ln y_3} \right) \right]}{[(1+y_2\epsilon_2)(y_4\epsilon_{34}) - (y_4\epsilon_{24})(y_2\epsilon_{23})]} \right] \quad (12)$$

Again, similar equations to that of (12) may be obtained for  $\Gamma_3$  and  $\Gamma_4$ .

The equations such as (12) are general under the given conditions. No approximations have been utilized and such relations may be obtained for (n-1) components of an n component system.

We take the special condition, at this time, of allowing the concentrations of components 3 and 4 to approach zero. For this case one obtains from Eq. (12) and the similar equations for  $\Gamma_3$  and  $\Gamma_4$  the relations

$$\Gamma_2 = -\frac{1}{RT} \left[ \frac{\left( \frac{\partial \sigma}{\partial \ln y_2} \right) - y_2\epsilon_{23} \left( \frac{\partial \sigma}{\partial \ln y_3} \right) - y_2\epsilon_{24} \left( \frac{\partial \sigma}{\partial \ln y_4} \right)}{(1 + y_2\epsilon_2)} \right]_{y_3, y_4 \rightarrow 0} \quad (13)$$

$$\Gamma_3 = -\frac{1}{RT} \left[ \left( \frac{\partial \sigma}{\partial \ln y_3} \right) \right]_{y_3, y_4 \rightarrow 0} \quad (14)$$

$$\Gamma_4 = -\frac{1}{RT} \left[ \left( \frac{\partial \sigma}{\partial \ln y_4} \right) \right]_{y_3, y_4 \rightarrow 0} \quad (15)$$

Substitution of Eqs. (14) and (15) in Eq. (13) gives



$$\Gamma_2 = - \left[ \frac{\left( \frac{\partial \sigma}{\partial \ln y_2} \right)}{RT(1+y_2\epsilon_2)} - \frac{(y_2\epsilon_{23}\Gamma_3 + y_2\epsilon_{24}\Gamma_4)}{(1+y_2\epsilon_2)} \right] \quad y_3, y_4 \rightarrow 0 \quad (16)$$

Similarly if one allows  $y_2$  and  $y_3$  to approach zero one obtains for  $\Gamma_4$

$$\Gamma_4 = - \left[ \frac{\left( \frac{\partial \sigma}{\partial \ln y_4} \right)}{RT(1+y_4\epsilon_4)} - \frac{(y_4\epsilon_{24}\Gamma_2 + y_4\epsilon_{34}\Gamma_3)}{(1+y_4\epsilon_4)} \right] \quad y_2, y_3 \rightarrow 0 \quad (17)$$

and finally if  $y_2$  and  $y_4$  approach zero one obtains for  $\Gamma_3$

$$\Gamma_3 = - \left[ \frac{\left( \frac{\partial \sigma}{\partial \ln y_3} \right)}{RT(1+y_3\epsilon_3)} - \frac{(y_3\epsilon_{23}\Gamma_2 + y_3\epsilon_{34}\Gamma_4)}{(1+y_3\epsilon_3)} \right] \quad y_2, y_4 \rightarrow 0 \quad (18)$$

Comparison of Eqs. (16), (17) and (18) with Eq. (7) shows that adsorption in a quaternary system results in a rather simple extension of the ternary relations.

For an  $n$  component system where  $n \geq 3$ , generalization of equations such as (16), (17) and (18) with component 1 taken as the solvent is given as

$$\Gamma_1 = - \left[ \frac{\left( \frac{\partial \sigma}{\partial \ln y_1} \right)}{RT(1+y_1\epsilon_1)} - \sum_{\substack{j=2 \\ j \neq i}}^n \frac{y_i\epsilon_{ij}\Gamma_j}{(1+y_i\epsilon_i)} \right] \quad \begin{matrix} y_j, s \rightarrow 0 \\ i = 2, 3, 4 \dots n \end{matrix} \quad (19)$$

Thus, one has available in Eq. (19) a relation which allows one to indicate the course of adsorption of a component in a multicomponent system. Should more than two of the components be present in concentrations above the dilute solution range, then recourse to more complete expressions, such

as Eq. (12), is necessary. Of course, the use of Eq. (12) would present a formidable task in terms of accumulating the necessary parameters for evaluation; however, equations such as Eqs. (16-18), as summarized in Eq. (19), are somewhat less complex and permit at least a guide to the adsorption in multicomponent systems. Bulk interaction coefficients are sometimes available and adsorption in dilute binary solutions are also sometimes available. Thus, adsorption behavior in multicomponent systems may be approximated via Eq. (19) which is certainly of aid in comparison to not having any scientific guide. In addition, in view of the recent growth of a variety of surface analytical tools, e.g. AES, LEED, UPS, ESCA, FIM, ISS, etc., particular systems where adsorption is of prime concern may well be studied quite thoroughly.

#### Discussion

The convenience of these type of adsorption equations was already indicated by Darken and Simkovich. In particular, it was noted that in a ternary system Equations (7a) and (7b) allow one to deduce whether adsorption of a specific component in a binary system may be enhanced or reduced by the presence of a third component as is reflected in the signs of  $\epsilon_{23}$  and  $\Gamma_2$  (or  $\Gamma_3$ ). Whenever  $\epsilon_{23}$  is of negative sign and  $\Gamma_2$  (or  $\Gamma_3$ ) is of reasonable magnitude then enhanced adsorption, perhaps beyond a monolayer, may be anticipated. Conversely, a positive sign on  $\epsilon_{23}$  indicates a dislike of 2 for 3 (and 3 for 2) in the solvent and again with a reasonable magnitude for  $\Gamma_2$  (or  $\Gamma_3$ ) the adsorption amounts may be reduced in comparison to a binary.

Of interest also is the sign of  $\Gamma_2$  (or  $\Gamma_3$ ) in Eq. (7) and the sign of  $(\partial\sigma/\partial\ln y_1)$  for it is entirely conceivable that  $\epsilon_{23}$  carries one sign, i.e., positive or negative, while  $\Gamma_2$  (or  $\Gamma_3$ ) may carry the opposite sign. On such

an occasion even though the first term on the right hand side of Eq. (7) is positive, as reflected by a negative value of  $\partial\sigma/\partial\ln y_i$ , the second term will reduce the adsorption amount.

In respect to multicomponent systems, as generalized in Eq. (19), each term and the parameters  $\epsilon_{ij}$  and  $\Gamma_j$  must be evaluated to determine the adsorption of component  $i$  in the system. If sufficient thermodynamic data ( $\epsilon_{ij}$ 's) are available and reasonable estimates of  $\partial\sigma/\partial\ln y_i$  and  $\Gamma_j$  may be made, one can then at least approximate the adsorption of  $\Gamma_i$  as a function of alloy composition.

Support by the U.S. Army Research Office is gratefully acknowledged.